

**Appl. No. 10/657,585**

**Response dated December 16, 2005**

**Reply to Final Office Action of October 17, 2005**

### **Amendments to the Claims**

This listing of claims will replace all prior versions, and listings, of claims in the application:

### **Listing of Claims:**

1. (Currently Amended) A method of making a catalyst support comprising
  - a) applying at least one compound of a rare-earth metal to an aluminum-comprising material to provide a rare-earth modified alumina precursor;
  - b) drying the rare-earth modified alumina precursor under suitable conditions to provide a dried rare-earth modified alumina precursor; and
  - c) calcining the dried rare-earth modified alumina precursor in a manner effective for converting at least a portion of the aluminum-comprising material to an alumina comprising at least one alumina phase selected from the group consisting of delta-alumina, theta-alumina, and combination thereof; and creating a surface coverage comprising an oxide of said rare-earth metal, wherein said surface coverage coats the alumina at least partially, and wherein one rare-earth metal is essentially trivalent, and further wherein the surface coverage is between about 0.2 nm and about 0.5 nm in thickness.
  
2. (Original) The method according to claim 1 wherein the aluminum-comprising material comprises at least one material selected from the group consisting of aluminum oxides, aluminum salts, aluminum alkoxides, aluminum hydroxides, pseudoboehmite, boehmite, gibbsite, bayerite, gamma-alumina, theta-alumina, delta-alumina, eta-alumina, rho-alumina, chi-alumina, kappa-alumina and any combinations thereof.
  
3. (Original) The method according to claim 1 wherein the aluminum-comprising material comprises a gamma-alumina.
  
4. (Original) The method according to claim 3 wherein the gamma-alumina has a surface

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area between about  $100 \text{ m}^2/\text{g}$  and about  $300 \text{ m}^2/\text{g}$ ; and a pore volume of at least about  $0.2 \text{ ml/g}$ .

5. (Original) The method according to claim 3 wherein the gamma-alumina comprises no more than about 0.1% by weight  $\text{Na}_2\text{O}$ .
6. (Original) The method according to claim 1 wherein the compound of the rare-earth metal comprises a counterion selected from the group consisting of nitrate, acetate, oxalate, acetylacetonate, any alkanoate, any halide and sulfate.
7. (Original) The method according to claim 6 wherein the compound of the rare-earth metal is in a hydrated form.
8. (Original) The method according to claim 1 wherein the rare-earth metal is selected from the group consisting of yttrium, lanthanum, praseodymium, neodymium, samarium and gadolinium.
9. (Original) The method according to claim 1 wherein applying a compound of the rare-earth metal is carried out by an impregnation technique.
10. (Original) The method according to claim 9 wherein the impregnation technique is performed at about or below ambient pressure.
11. (Original) The method according to claim 9 wherein the impregnation technique is incipient wetness impregnation.
12. (Canceled)
13. (Original) The method according to claim 1 wherein calcining is effective for creating a rare-earth metal oxide surface layer that completely covers the alumina surface.

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14. (Original) The method according to claim 1 wherein calcining is effective for converting at least a portion of the aluminum-comprising material to a transition alumina comprising theta-alumina.

15. (Original) The method according to claim 1 wherein calcining is performed at a temperature between about 800 °C and about 1,400 °C.

16. (Original) The method according to claim 15 wherein calcining is performed at a temperature between about 1,000 °C and about 1,300 °C.

17. (Original) The method of making a catalyst support according to claim 1 further comprising applying at least one compound of another rare-earth metal.

18. (Original) The method according to claim 17 wherein the application of at least one compound of another rare-earth metal is performed simultaneously to step a).

19. (Original) The method according to claim 17 wherein the application of at least one compound of another rare-earth metal is performed after step c).

20. (Original) The method according to claim 19 further comprising calcining at a temperature between about 300 °C and 900 °C.

21. (Currently Amended) A rare-earth oxide modified catalyst support comprising  
an alumina material comprising optionally gamma-alumina, and an alumina phase  
selected from the group consisting of theta-alumina, delta-alumina, eta-alumina, rho-alumina,  
chi-alumina, kappa-alumina, and any combinations thereof; and  
a surface coverage comprising an oxide of at least one rare-earth metal, wherein said  
coverage coats the alumina material at least partially, and wherein one rare-earth metal is

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essentially trivalent,

wherein the support does not substantially degrade in the presence of mildly acidic conditions comprising a pH equal to or greater than about 4.

22. (Previously presented) The catalyst support according to claim 21 wherein the support comprises at least one alumina phase selected from the group consisting of delta-alumina, theta-alumina and combination thereof.

23. (Previously presented) The catalyst support according to claim 21 wherein the support comprises theta-alumina.

24. (Original) The catalyst support of claim 21 wherein the trivalent rare-earth metal is selected from the group consisting of yttrium, lanthanum, praseodymium, neodymium, samarium, and gadolinium.

25. (Original) The catalyst support of claim 21 wherein the trivalent rare-earth metal is present in an amount between about 1% and about 15% by weight of metal to final weight of modified support.

26. (Original) The catalyst support according to claim 21 wherein the surface coverage comprising an oxide of at least one trivalent rare-earth metal coats the alumina phase completely.

27. (Original) The catalyst support according to claim 21 further comprising a structural modifier comprising a metal selected from the list consisting of elements of Groups 1-17 of the Periodic Table.

28. (Original) The catalyst support according to claim 27 wherein the structural modifier comprises an element selected from the group consisting of boron, magnesium, silicon, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, strontium, zirconium,

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molybdenum, tin, and barium.

29. (Original) The catalyst support according to claim 21 wherein the support is characterized by

a surface area between about 40 m<sup>2</sup>/g and about 150 m<sup>2</sup>/g; and  
a pore volume between about 0.1 cm<sup>3</sup>/g and about 0.5 cm<sup>3</sup>/g.

30. (Previously presented) The catalyst support of claim 21 wherein the support undergoes a phase transformation to at least one alumina phase selected from the group consisting of delta-alumina, theta-alumina, and combination thereof, at a temperature that is higher than that found for the transformation of an unmodified gamma-alumina to at least one alumina phase selected from the group consisting of delta-alumina, theta-alumina, and combination thereof.

31. (Canceled)

32. (Currently Amended) A Fischer-Tropsch catalyst comprising  
at least one catalytically active metal comprising cobalt, wherein the cobalt metal is dispersed in crystallites having an average size of between about 5 nm and about 20 nm;  
optionally, at least one promoter; and  
a rare-earth oxide modified catalyst support including  
at least one alumina material comprising an alumina phase selected from the group consisting of delta-alumina, theta-alumina, and combination thereof; and optionally gamma-alumina; and  
a surface coverage comprising an oxide of at least one rare-earth metal, wherein said coverage coats the alumina material at least partially, and wherein one rare-earth metal is essentially trivalent.

33. (Canceled)

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**34. (Original)** The catalyst of claim 32 wherein the catalytically active metal is present in an amount between about 1% and about 50% by weight of metal to final weight of catalyst.

**35. (Original)** The catalyst of claim 32 wherein the promoter comprises one element from Groups 1-14 of the Periodic Table of Elements.

**36. (Canceled)**

**37. (Currently amended)** The catalyst of claim 36 32 wherein the promoter comprises at least one metal selected from the group consisting of platinum, palladium, silver, ruthenium, iridium, rhodium, and rhenium.

**38. (Currently amended)** The catalyst of claim 36 32 wherein the cobalt metal is dispersed in crystallites arranged on the surface coverage comprising at least one trivalent rare-earth metal oxide.

**39-41. (Canceled)**

**42. (Original)** The catalyst according to claim 32 wherein the trivalent rare-earth metal is selected from the group consisting of yttrium, lanthanum, praseodymium, neodymium, samarium and gadolinium.

**43. (Original)** The catalyst of claim 32 wherein the rare-earth oxide modified catalyst support further comprises a structural modifier, and said structural modifier comprises one element selected from the group consisting of boron, magnesium, silicon, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, strontium, zirconium, molybdenum, tin, and barium.

**44. (Previously Presented)** The Fischer-Tropsch catalyst according to claim 32 wherein the

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Fischer-Tropsch catalyst is used to practice any process for converting a reactant gas mixture comprising synthesis gas under suitable conditions to a product mixture comprising linear hydrocarbons.

**45. (Original)** The Fischer-Tropsch catalyst according to claim 44 wherein the conditions suitable for converting a reactant gas mixture comprise a temperature no less than 160 °C and a pressure no less than about 5 atm.

**46. (Previously Presented)** The Fischer-Tropsch catalyst according to claim 45 further comprising no more than about 10 mol% aluminate spinels comprising the catalytically active metal before, during or after said process.

**47. (Original)** The Fischer-Tropsch catalyst according to claim 45 wherein the alumina that comprises the support retains its original phase upon exposure to said process.

**48. (Original)** The Fischer-Tropsch catalyst according to claim 45 wherein the promoter retains a majority of its original activity upon exposure to said process.

**49. (Currently Amended)** A method of making a Fischer-Tropsch catalyst comprising applying at least one compound of a catalytically active metal to a rare-earth oxide modified catalyst support to form a catalyst precursor, wherein the rare-earth oxide modified catalyst support includes

at least one alumina material comprising an alumina phase selected from the group consisting of theta-alumina, delta-alumina, eta-alumina, rho-alumina, chi-alumina, kappa-alumina, and any combinations thereof; and optionally gamma-alumina; and

a surface coverage comprising an oxide of at least one rare-earth metal, wherein said coverage coats the alumina material at least partially, and wherein one rare-earth metal is essentially trivalent;

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calcining said catalyst precursor; and  
reducing calcined catalyst precursor to form a reduced catalyst; and further  
embedding the reduced catalyst in oil or solid hydrocarbon.

**50. (Canceled)**

**51. (Original)** The method of claim 49 wherein the trivalent rare-earth metal is selected from the group consisting of yttrium, lanthanum, praseodymium, neodymium, samarium and gadolinium.

**52. (Original)** The method of claim 51 wherein the rare-earth oxide modified catalyst support comprises between about 1 wt% and about 15 wt% of rare-earth metal.

**53. (Original)** The method of claim 49 wherein the rare-earth oxide modified catalyst support comprises an alumina phase containing essentially theta-alumina.

**54. (Original)** The method of claim 49 wherein applying at least one compound of a catalytically active is done by impregnation.

**55. (Original)** The method of claim 49 wherein the catalytically active metal comprises cobalt.

**56. (Original)** The method of claim 55 wherein the catalyst comprises between about 5 and about 40% cobalt.

**57. (Original)** The method of claim 55 wherein the compound of the catalytically active metal comprises cobalt nitrate, cobalt nitrate hexahydrate, cobalt acetate, cobalt acetylacetonate, or combinations thereof.



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58. (Original) The method of claim 49 wherein the catalytically active metal comprises iron.

59. (Original) The method of claim 49 further comprising applying a compound of a promoter.

60. (Original) The method of claim 59 wherein the compounds of catalytically active metal and of the promoter are applying simultaneously by impregnation.

61. (Original) The method of claim 59 wherein the catalytically active metal is cobalt and the promoter comprises at least one metal selected from the group consisting of platinum, palladium, silver, ruthenium, iridium, rhodium, and rhenium.

62. (Original) The catalyst of claim 59 wherein the catalytically active metal is iron, and the promoter comprises at least one metal selected from the group consisting of sodium, copper, potassium, lithium, and silver.

63. (Currently amended) A process for converting synthesis gas to hydrocarbons, wherein the process comprises

converting a reactant gas mixture comprising hydrogen and carbon monoxide under conditions effective for producing a product mixture comprising waxy paraffinic hydrocarbons over a hydrocarbon synthesis catalyst comprising

at least one catalytically active metal comprising cobalt, wherein the cobalt metal is dispersed in crystallites having an average size of between about 5 nm and about 20 nm;

optionally, at least one promoter; and

a rare-earth oxide modified catalyst support comprising

an alumina material comprising optionally gamma-alumina, and at least one alumina phase selected from the group consisting of delta-alumina, theta-alumina, and any combination thereof; and

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a surface coverage comprising at least one rare-earth metal oxide, wherein one rare-earth metal is essentially trivalent, and wherein said coverage coats the alumina material at least partially.

64. (Original) The process according to claim 63 wherein the reactant gas mixture has a  $H_2:CO$  ratio between 0.67:1 and 5:1.

65. (Original) The process according to claim 63 wherein the reactant gas mixture has a  $H_2:CO$  ratio between 1.4:1 and 2.3:1.

66. (Currently Amended) The process according to claim 63 wherein the waxy paraffinic hydrocarbons comprise mostly linear hydrocarbons having at least 18 carbon atoms.

67. (Original) The process according to claim 63 wherein the process has a selectivity for hydrocarbons products characterized by an alpha value of at least 0.85.

68. (Original) The process according to claim 63 wherein the process produces methane and has a methane selectivity not more than about 10 wt%.

69. (Original) The process according to claim 63 wherein the waxy hydrocarbons contain no more than 100 ppm of catalytically active metal.

70. (Original) The process of claim 63 wherein the catalytically active metal is cobalt.

71. (Original) The process of claim 70 wherein the hydrocarbon synthesis catalyst comprises a promoter and said promoter comprises at least one metal selected from the group consisting of platinum, palladium, silver, ruthenium, iridium, rhodium, and rhenium.

72-73. (Canceled)

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**74.** (Original) The process according to claim 63 wherein the rare-earth metal is selected from the group consisting of yttrium, lanthanum, praseodymium, neodymium, samarium and gadolinium.

**75.** (Currently amended) The ~~method of~~ process according to claim 63 wherein the rare-earth oxide modified catalyst support comprises between about 1 wt% and about 15 wt% of rare-earth metal.

**76.** (New) The catalyst of claim 32 wherein the catalyst comprises between about 5 and about 40% cobalt.

**77.** (New) The method of claim 55 wherein the cobalt metal is dispersed in crystallites having an average size of between about 1 nm and about 20 nm.

**78.** (New) The method of claim 55 wherein the cobalt metal is dispersed in crystallites having an average size of between about 5 nm and about 20 nm.